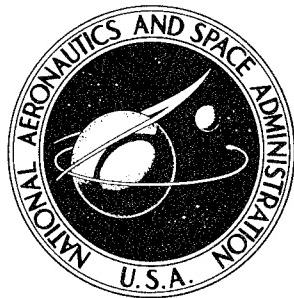


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FOR SPACE APPLICATIONS

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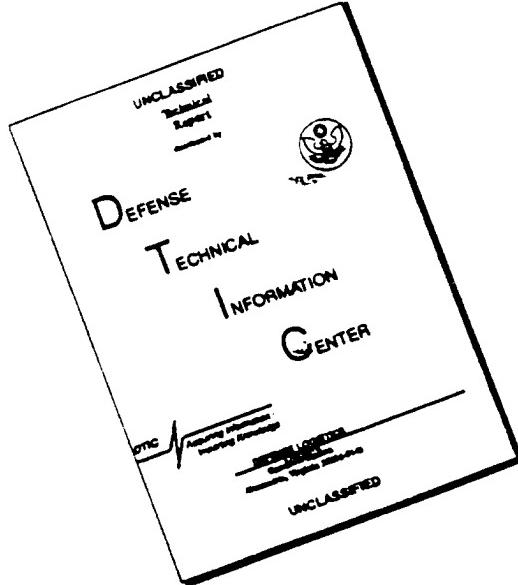
San Diego, Calif.

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1967

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FIBROUS REINFORCEMENTS FOR SPACE APPLICATIONS

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ABSTRACT

The properties of several polymeric materials obtained from a review of available data were defined and tabulated. Information on the polymeric material for both film and fiber forms, where available, was tabulated. Potential polymer classes for further development as materials for space applications have been identified.

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SECTION I

INTRODUCTION

The new classes of polymers developed during the past few years impart unique properties upon structural materials. The new polymeric materials are used in applications throughout the spectrum of working temperatures, from the rocket nozzles exhaust to cryogenic tankage environments. Certain polymeric materials successfully withstand exposure to the hostile environment of space, where high vacuum, radiation, and micrometeoroid impact tend to degrade materials.

In order to determine the effectiveness of the various polymeric materials for potential space applications, the properties and possible applications of different polymeric materials were surveyed. The availability of information on the different polymer classes was, as would be expected, dependent upon many factors, including the length of time since pilot production and the form in which the material had been produced. If the polymeric material were produced primarily as a film, properties such as tensile strength, permeability, and flexibility were emphasized. Feasibility studies and actual hardware fabrication of expandable structures have indicated new applications for structural flexible materials. These applications require fibrous materials which exhibit the flexibility needed for folding and packaging yet maintain a structural capability in the expanded state.

In order to determine the properties and potential of the different polymeric families, several general guidelines were established to minimize the complexity of obtaining this information. These guides, used throughout the investigation, are listed below.

1. The polymer classes were set up based on materials whose development had progressed beyond the point of initial laboratory synthesis.
2. The properties were reported as a range of values and not as a single value. This was considered to be more meaningful, as the wide variation in properties of polymeric materials is apparently due to differences in proprietary process by the producers.
3. Only room temperature properties at standard environment were tabulated for this report. The lack of standard test methods for environmental testing prevented a correlation of data from different sources. This lack of standardization was particularly noticeable in the areas of vacuum and ultraviolet testing.

SECTION II

REVIEW AND RATING OF POLYMER CLASSES

Polymers were selected from a preliminary list of 22 polymer families. This general classification served as the starting point for the material selection. This compilation, presented as Table I, included various available forms of the polymers, such as moldings, fibers, films, and foams. Each form of the material may have various applications.

Table 1 describes the polymer type, forming reaction, and principal advantages and disadvantages. The type of polymer is classed as either thermoplastic, thermosetting, or nonmelting. There may be two types of the same polymer, depending on the type of forming reaction employed.

The polymer forming reaction is either the addition or condensation type. Addition polymer reaction produces the polymer as the sole product. On the other hand, the condensation polymerization yields a polymer and a secondary product which is usually in the form of a volatile material.

The various sources used for obtaining the information included Chemical Abstracts, Technical Abstract Bulletin (TAB), Scientific and Technical Aerospace Reports (STAR), and Modern Plastics Encyclopedia for 1966, and provided the starting point for obtaining the information of the different classes of polymers. The general headings used in the abstracts are listed in Table 2.

The abstracting services of the Defense Documentation Center (DDC) were used to obtain a report bibliography entitled "Materials for Spacecraft Applications."

The literature on material characteristics and properties was compiled from these sources, and is presented in Appendix I.

Manufacturers of various polymers were also contacted in an attempt to obtain pertinent information on their product. With only a few exceptions, unfortunately, they were reluctant to cooperate, probably because of proprietary reasons.

Inasmuch as the task of compiling information for all the polymer classes listed in Table 1 would have been beyond the frame of this study, a system of selecting several polymer classes was used. A numerical rating was established for each of several properties for the different polymer classes. A rating of 3 indicated that the polymer had good properties or resistance to a given condition; a rating of 2 indicated that properties were satisfactory; and a rating of 1 indicated unsatisfactory performance in the designated area.

The physical and mechanical properties used for the rating included tensile strength and modulus, and toughness at room temperature. The polymer was also judged on its capability of continuous use at both 500°F and cryogenic temperatures. These properties were considered to be representative of the mechanical properties required of a potential polymer for space usage. The different polymer classes were also rated in terms of the effect of vacuum exposure and

TABLE 1
GENERAL CLASSES OF POLYMERS

Polymer	Type	Polymer Forming Reaction	Unique Advantages	Unique Disadvantages	Applications
<u>Acrylics</u> (including styrene-modified acrylics)	Thermoplastic	Addition	Processing ease, transparency, good dielectric strength, resistance to weathering, RT	Tends to "unzip" in decomposition reactions, soluble in methyl ethyl ketone, etc.	Coatings, fibers, composites, molding, transparency
<u>Allylics</u>	Thermosetting	Addition	Imparts formulation versatility to acrylics and unsaturated polyesters	Not much utility when used alone	Composites, molding
<u>Polyesters</u> (Saturated) (Unsaturated)	Thermoplastic	Condensation	Highest tensile strength now available in films	Completely destroyed by ammonia	Fibers, films
	Thermosetting	Addition	Rapid cures possible. Very processable. RT cures	Similar to acrylics	Composites
<u>Polyamides</u> (including poly-peptides)	Thermoplastic or nonmelting	Condensation or addition	Very low coefficient of friction	Absorbs water, which reduces physical properties	Fibers, molding
<u>Polyethers</u>	Thermoplastic	Addition	Used for thickeners and water-soluble films	Water soluble	Films, molding
<u>Oxide-derived</u>	Thermoplastic	Addition	Low coefficient of friction	Poor resistance to acid and base	Films, molding
<u>Acetals</u>	Thermoplastic	Addition	Transparency	Soluble in polar organic solvents	Films, molding
<u>Phenoxy</u>	Thermoplastic	Addition			
<u>Epoxyes</u>	Glycidyl ethers and epoxy novolacs	Thermosetting	Wide selection of curing agents. Very processable. Good adhesion. RT cures are possible	Complete utilization of functionality is difficult	Coatings, composites, filament winding, coatings, adhesives
<u>Fluorocarbons</u>	Thermoplastic or nonmelting	Addition	Generally good electrical properties. Inert. Good solvent resistance	Density higher than usual polymer (1.7). Thermal decomposition products are highly toxic	Film, fiber, release agents, molding

TABLE 1 (Continued)

Polymer	Type	Polymer Forming Reaction	Processing Advantages	Unique Disadvantages	Applications
<u>Polyolefins</u>					
Polyethylene	Thermoplastic	Addition	Low cost	Difficult bonding. Low melt temperature	Film, fibers, molding
Polypropylene	Thermoplastic	Addition	Low cost	Difficult bonding. Low melt temperature	Film, fibers, molding
Ionomer	Thermoplastic	Addition	Transparency	Difficult bonding. Low melt temperature	Film, fibers, molding
High molecular weight polyethylene	Nonmelting	Addition	Unusual cryogenic strength	Difficult bonding. No fibers	Film, molding
<u>Polyaromatics</u>					
Polyphenylene	Very high melting and thermoplastic	Condensation	Aromatic ethers have good solubility	--	Composites
Polyxylylenes	Very high melting and thermoplastic	Condensation	--	--	Composites
Polyphenylethers	Very high melting and thermoplastic	Condensation	Very low dielectric loss	Opaque	Composites
<u>Silicones</u>	Thermosetting	Condensation or addition	Several RTV's available	Low physical properties, especially in elastomeric materials	Elastomers, composites, sealants, release agents
<u>Vinyls</u>	Thermoplastic	Addition	Generally well suited to commercial high-volume molding	Tends to "unzip" in decomposition reactions. Many are soluble in methyl ethyl ketone	Fibers, films, molding, foams
<u>Cellulosics</u>					
Acetate	Thermoplastic or nonmelting	Condensation	Inexpensive	Soluble in organic solvents	Fibers, films, molding
Regenerated cellulose	Nonmelting	Condensation	Unusual structure contributes to high performance	Subject to mildew	Fibers, fabrics

TABLE 1 (Continued)

Polymer	Type	Polymer Forming Reaction	Unique Advantages	Unique Disadvantages	Applications
<u>Polyurethanes</u> (Including epoxy polyurethanes)	Thermoplastic, thermosetting	Addition	Low permeability. Good abrasion resistance. Rapid cure. Epoxy polyurethanes solvent resistant. Very high hysteresis	Prepolymers are water sensitive. Short pot life. Epoxy polyurethanes are new; little data	Elastomers, films, fibers, adhesives, foams, coating
<u>Polyheterocyclics</u>	Normelting	Condensation	High char yield in ablation	Processing requires high temperature. High volatile content	Composites, fibers, film, adhesives, coating
<u>Phenolics</u>	Thermosetting	Condensation	Wide selection of prepolymers. (Fesoles and novolacs).	Always a highly cross-linked rigid polymer system.	Molding, composites, adhesives
<u>Polycarbonates</u>	Thermoplastic	Condensation	Self-extinguishing. Transparent. Perhaps best polymer for impact strength	Rapid water pickup. Soluble in aromatic hydrocarbons and chlorocarbons	Film, moldings for impact resistance
<u>Urea</u> (Formaldehyde and melamine formaldehyde)	Thermosetting	Condensation	Good compressive strength	Generally not useful without fillers or reinforcements	Molding
<u>Polysulfides</u>	Thermosetting	Addition	RTV's available	Poor physical properties	Sealant, potting compounds
<u>Polysulfones</u>	Thermoplastic	Addition	Improved creep resistance at moderate temperatures. Transparent. Self-extinguishing	Soluble in aromatic hydrocarbons and chlorohydrocarbons	Films, molding
<u>Ladders, Step Ladders</u>	Normelting	Condensation	Double-strand polymer has better physical retention during severe environmental exposure	Commercially unavailable. Very new system	High-temperature applications
<u>Glass</u>	Thermoplastic	Condensation			
<u>Inorganics</u>	Thermosetting & normelting	Condensation	Not dependent on C-C bonds, so greater bond energies possible	Commercially unavailable. New system. Difficult processing.	

TABLE 2
ABSTRACT HEADINGS FOR LITERATURE SURVEY

Abstract Source		
Chemical Abstracts	TAB	STAR
Radiation; effect on polymers	Organic coatings; degradation of	Space radiation; effect of
Polymers; aging of radiolysis of radiation effect on radiation resistance of stress-temperature properties of space effects on	Space environment conditions; Polymers; space effects on radiation effects on thermal properties of	Space environment Space suit; materials for Radiation effects Polymers Depolymerization Space vehicles; materials for (adhesives, coatings) Vacuum; effect on (polymers)

radiation stability. A final rating factor was polymer fiber forming capability. The assigned rating and the total for each polymer class is presented in Table 3.

Polymer classes were selected based on the total rating for the class in general. The following polymer classes had the highest rating and were thus chosen for further investigation:

<u>Class</u>	<u>Rating</u>
Polyheterocyclics	23
Ladders, Step Ladders	21
Polyaromatics (Polyxylylenes)	20
Cellulosics (Regenerated)	19
Fluorocarbons	19
Polyaromatics (Polyphenylenes)	19
Polyesters (Saturated)	18
Polyamides	17
Polyurethanes	17
Polyolefin (Polypropylene)	17

TABLE 3
RATINGS OF POLYMER FAMILIES

Polymers	RT Tensile Strength	RT Modulus	RT Toughness	High-Temp* Capability	Cryogenic Capability	Vacuum Exposure	Radiation Stability	Fiber Formability	Total Rating
<u>Acrylics</u> (Including styrene-modified acrylics)	3	3	1	1	1	1	1	3	14
<u>Allylics</u>	2	2	1	1	1	2	1	2	12
<u>Polyesters</u> (Saturated)	3	3	1	1	3	3	1	3	18
(Unsaturated)	3	3	2	1	1	3	1	3	17
<u>Polyamides</u> (Including polypeptides)	3	2	3	1	1	3	1	3	17
<u>Polyethers</u> Oxide derived	1	1	1	1	3	3	1	1	12
Acetals	3	3	2	1	2	1	1	1	14
Phenoxy	2	2	3	1	1	3	2	2	16
<u>Epoxyes</u> (Glycidyl ethers and epoxy novolacs)	3	2	1	1	1	3	2	1	14
<u>Fluorocarbons</u>	2	1	2	2	3	3	3	3	19
<u>Polyolefins</u> Polypropylene	3	2	3	1	2	2	1	3	17
Polyethylene ionomer	2	1	3	1	1	2	1	3	14
High molecular weight polyethylene	2	1	3	1	3	2	1	1	14
<u>Polyaromatics</u> Polyphenylenes	3	3	1	1	3	3	3	2	19
Polyxylylenes	3	3	1	3	2	3	3	2	20
Polyphenylethers	3	2	1	2	1	3	1	1	19
<u>Silicones</u>	1	1	1	2	1	3	1	1	11

* Continuous capability at 500°F.

TABLE 3 (Continued)

Polymers	RT Tensile Strength	RT Modulus	RT Toughness	High-Temp* Capability	Cryogenic Capability	Vacuum Exposure	Radiation Stability	Fiber Formability	Total Rating
<u>Vinyls</u>	3	3	1	1	1	1	1	2	13
<u>Cellulosics</u>									
Acetate	2	2	1	1	3	3	1	3	16
Regenerated cellulose	3	3	3	1	2	3	1	3	19
<u>Polyurethanes</u>	3	1	2	1	3	3	1	3	17
Epoxy polyurethanes	3	2	2	1	2	3	1	1	15
<u>Polyheterocyclics</u>	3	3	2	3	3	3	3	3	23
<u>Phenolics</u>	2	3	1	2	2	3	2	2	16
<u>Polycarbonates</u>	2	2	3	1	1	3	2	2	16
<u>Urea</u> (Including formaldehyde, melamine formaldehyde)	1	3	1	1	1	3	1	1	12
<u>Polysulfides</u>	1	1	1	1	1	2	1	1	9
<u>Polysulfones</u>	3	2	1	1	1	3	2	1	14
<u>Ladders, Step Ladders</u>	2	3	2	3	3	3	3	2	21
<u>Glass</u>	3	3	1	3	3	3	3	3	22
<u>Inorganics</u>	1	3	1	3	1	3	3	1	16

* Continuous capability at 500°F.

Several polymer classes were divided further in order to include a wide range of available materials. Several subclasses were established in the fluorocarbon (polyfluorolefins) and polyamide polymer classes. The selected polymer classes and group subclasses are presented in Table 4, where identification is established by chemical name and polymer structure. To further identify the different polymers, trade names and sources or supplier are also presented. The polymeric materials were then classified by film, fiber, and general use categories. Some of the polymers were represented by more than one classification.

TABLE 4

SELECTED POLYMER FAMILIES

Polymer Class	Chemical Name	Structure	Trade Names	Sources	Remarks
		Film	Fiber	General	
Polyesters (Saturated)	Poly(ethylene terephthalate)		Mylar Kodel Scotchlite	DuPont Baram Others include Cordier Mycene Colman Aetna Enka	Many variations possible in both dolt & diacid moieties. Polyethylene terephthalate seems to represent some optimum in performance
Polyamides	Polyacrylamide Nylon 6		Capron Zytel 211 Plaskon	Allied Chemical duPont Nylyn-Allied	Picks up moisture & loses strength. Inexpensive
	Polyhexamethylene adipamide Nylon 6/6		--	Zytel 101	Excellent orientation effects in drawing. Readily adhered to.
	Polyhexamethylenesuccinamide Nylon 6/10		--	Zytel 31	Reduced water pickup
	Poly-11-aminoundecanoic acid Nylon 11		--	--	Foreign suppliers only Lower moisture absorption
Special mixed systems			--	Zytel 61 Plaskon 253	Generally used for special applications including formulated systems, i.e., adhesives, etc.
Aromatic polyamides			Hexam	--	High-temperature fabrics
Polyfluorolefins	Polytetrafluoroethylene		Teflon TFE	Allied Chemical duPont	Trade names of minor pro- ducers include "Tefran" Pennsalt, "Polyflon" Thiokol, "Fluon" ICI, "Algofton" Montecatini
	Copolymer of tetrafluoro- ethylene & hexafluoro- propylene		Teflon FEP	Teflon FEP	Thermoplastic upper tem- perature limit not as high as TFE
	Polychlorotrifluoroethylene		Kel-F 81 Aclar	--	Trade names of minor pro- ducers include "Tefran" Pennsalt, "Polyflon" Thiokol, "Fluon" ICI, "Algofton" Montecatini
	Copolymer of tetrafluoro- ethylene & vinylidene fluoride		Viton Fluorel	--	Some of these are modified with vinylidene fluoride
	Polyvinylidene fluoride		--	Kynar	Usually elastomeric in nature & can be modified by formulating (curing agents, fillers, etc.)
	Polyvinyl Fluoride		Tedar	--	
Regenerated Cellulose	Cellulose (Glucose-β-glucoside)		--	Fortisan Rayon	Material has low per- meability
				--	Denter available: 30, 90, 270. Fortisan 36 no longer available as a high- strength fiber. Fortisan tends to break when subjected to high modulus.
				--	Various suppliers
					No water pickup, mildew

TABLE 4 (Continued)

Polymer Class	Chemical Name	Structure	Trade Names Film	Fiber	General Sources	Remarks
Polyurethanes			-- Estate -- Special Form "Spandex" ADM	-- Adiprene Toxin etc. Arolast Customer Centthane	du Pont Goodrich Hobay du Pont & others Isocyanate Products General Tire	A wide variety of structures & modifications possible. High abrasion resistance.
Ladders & Step Ladders	Polybis(benzimidazole)-Benzodipyrrolidone		--	--	Pyrone	Whittaker Corporation San Diego, California NASA Langley Development
Polyhetrocyclics	Polyimide		Kaptun (K-111m)	--	Vespel Sigray	Molding system not available. Cost \$5-15/lb
	Polybenzimidazole		-- Ar = aromatic ring system	--	du Pont Mononanto	Molding system not available. Cost \$5-15/lb
Polyaromatics	Polyphenylene		-- AF contract	--	Calenese	Forms good composite structures. Useful in ablation. Processing requires high temperature.
	Polypolylylene		-- C1	--	Whittaker Corporation San Diego, California	Films not available unless high-temperature performance is compromised. Cost \$80-\$100/lb
	Polyphenylene ether		--	--	Eitel McCullough Inc., San Carlos, California	New material. Available only in powder form. Requires unusual processing. Cost \$300/lb

SECTION III

DESCRIPTION OF THE SELECTED POLYMERS

The selected polymers are described in the following sections. The general polymer characteristics are discussed. The current and past work accorded to the polymer is also described. The current work as reported by the various industrial and Governmental groups is reflected in the list of references for this report.

POLYESTERS (SATURATED)

Although this polymer class encompasses a multitude of possible variations, the general ratings shown in Table 4 refer to the most promising type of polymer, prepared from an aliphatic diol and an aromatic dibasic acid. The most widely accepted material is polyethyleneterephthalate.

Polyethyleneterephthalate is good to outstanding in the areas of strength, availability of various film (and fiber) weights (and weaves), and electrical properties. The thermal and radiation resistance is low enough to cast some doubt as to its general usefulness in a space environment without additional protection, however.

Structural modification is not a practical way to improve thermal stability, as the ester linkage present in all polyesters has lower thermal stability than other units of the polymer. The polymer can be protected from ionizing radiation, however, if a cyclic diol is used in place of the linear aliphatic diol. Cyclic diols offer an advantage in that the chain can be severed by radiation without a loss of molecular weight, as in the case of step ladder polymers.

Most of the development work on this polymer class has been conducted by industry. These fibers and films are primarily used, of course, for high-volume commercial applications. The presently available materials generally fill the needs of today's market, with new design applications occasionally requiring special processing.

Polyethyleneterephthalate has a serious disadvantage in that it does not bond well to the film unless the film is chemically pretreated. A few of the more recent reviews and test results for polyesters as well as many of the other classes of polymers were reviewed.¹⁻⁵

POLYAMIDES

This class of polymers, frequently referred to as nylons, represents one of the oldest types of synthetic organic polymers known; consequently, most area of developmental research are well explored.

Principal disadvantages include poor thermal stability and loss of physical properties because of water pickup. Advantages include excellent tenacity, low cost, and well-developed processing technology.

During the last 10 years, DuPont has been investigating completely aromatic polyamides. A new fiber (Nomex), whose structure is shown in Table 4, was the result of this effort.

Other textile fiber producers such as Celanese have also been working in this area, but significant breakthroughs have not been made. The subclass of aromatic polyamides does improve the 500°F rating (see Table 3). In addition, this subclass is not subject to moisture pickup, as evidenced by the aliphatic polyamides.

Within the polyamide class, the aromatic polyamides (e.g., Nomex) are probably close to the ultimate molecular structure for thermal stability and radiation resistance.

POLYFLUOROLEFINS

This classification covers fluorinated polyolefins containing only carbon, hydrogen, fluorine, and chlorine atoms. This includes the most common commercially available fluorinated polymers such as Teflon, Halon, Viton, Kynar, Kel-F, and Aclar. These fluorocarbon polymers have been fully developed by various commercial houses, but a considerable amount of research and development work is still being done both by these companies and by Government agencies.

All of the research being conducted or funded by Government agencies⁷⁻¹¹ is applications-oriented. This work is principally aimed at improving the high-temperature strength of the polyhydrofluorocarbons and polyperfluorocarbons. These polymers have exhibited superior aging properties in the temperature range from 400°F to 600°F, but their use has been severely hampered because of low strength at temperature.

Fibers have been made from extrudable Teflon FEP, but apparently no research is currently being conducted to improve these fibers. They have poor strength, especially at high temperatures.

Films of sheets have been made from all of the fluorocarbon and hydrofluorocarbon polymers. The permeability of some of these polymers is very low. Research has been carried out on plating Viton type elastomers with malleable or ductile metals which are resistant to powerful oxidizers and penetrating rocket fuels.¹²

Chemical resistance, low surface friction, and high internal damping are the most important properties these polymers have for use in structural space applications. However, the radiation resistance of this polymer is not as great as that of some of the other polymers.

The most needed improvement in polyfluorolefins seems to be in the area of processability. In Kel-F, Kynar, Viton, and Aclar, thermal properties and strength at temperature must be improved. These polymers are now well developed, with much work already completed. Some marginal improvement possibly can be realized, but it does not appear likely that research on these polymers will produce any immediate breakthrough of major significance.

REGENERATED CELLULOSE

Regenerated cellulose films have tensile strengths ranging from 7,000 psi to 10,000 psi (cellophane). Fibers exhibit strengths of 58,000-88,000 psi (for high-tenacity viscose rayon fiber) to 136,000-155,000 psi (for saponified cellulose acetate fiber). In addition to high tenacity, the fibers have a high crease resistance, dimensional stability, and high modulus values.

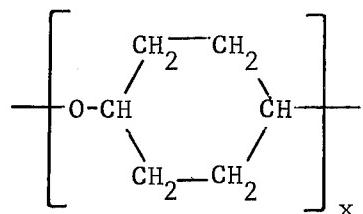
The high tenacity of the rayons, especially Fortisan, makes these materials very useful as reinforcements in composite structures where high tensile and impact strength is desired. One of the greatest disadvantages of this type of polymer is its decomposition temperature of 300°F. Improving its temperature resistance has been given considerable attention, but the basic weakness of the natural polymer still remains. At present, efforts are centered on improving properties of the fabric. This includes work to improve smoothness, residual shrinkage, elasticity, crease resistance, and fireproofing. However, any modification to the polymer structure that would benefit space applications may lower the tensile strength to such a degree that it would no longer be competitive with other polymers for space applications.

POLYURETHANES

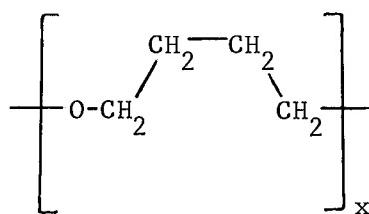
Polyurethanes are currently being selected for structural space applications, primarily on the basis of their excellent cryogenic performance. Polyurethanes have excellent tensile strength at -320°F. They may also find use in space bonding applications as they are generally fast-curing two-part systems, as demonstrated under various Government contract work.^{13, 14} Polyurethane rubbers are very abrasion resistant and can also be used at cryogenic temperatures for such applications as fuel seals and caulking compounds.

In the form of fibers or films, polyurethanes are very elastic. These elastic films are being considered for use as liners for filament-wound vessels or as expulsion bladders in fuel tanks. These films or fibers may also find application in expandable or inflatable space structures.

Major improvements which are needed in the polyurethane system include greater thermal, radiation, and oxidizer resistance. Increasing the aromatic character of the polymer may impart more heat resistance and presumably more radiation resistance, but only at great sacrifice to the low temperature properties and flexibility. Another possible way to improve heat resistance is to increase polyurea content. Using an isocyanatic-capped polyquinital polymer may also improve ionizing radiation resistance. This backbone offers the advantage of a step ladder polymer without appreciably changing the polytetrahydrofuran backbone, which displays excellent cryogenic properties:



Polyquinital



Polytetrahydrofuran

Work with fluorinated polyurethanes¹⁵ is being carried out to produce LOX-compatible polymers which may have greater heat and radiation resistance than the conventional polyurethanes.

POLYIMIDES

The polyimides are members of a relatively new class of synthetic polymers, the polyheterocyclics. These polymers offer potential as structural resins for rigid environmental conditions by virtue of their unique properties such as excellent hydrolytic, oxidative, and thermal stability. The polyimides are readily prepared from the reaction of commercially available aromatic dianhydrides and aromatic diamines in the form of processable precursor polymers, the polyamic acids. The polyamic acids are soluble and can be conveniently applied to the substrate and subsequently cured to final polymer. An important processing characteristic of the polyamic acids is the low volatile weight loss during cure. Many forms of polyimides are currently available commercially under various trade names such as DuPont's Kapton (H-film) or Monsanto's Skygard 700. Because they are all polyimides, however, all the polymers are chemically very similar and their properties differ only slightly. The polyimides have a large number of attractive features, which makes them the most popular polyheterocyclic currently available. These features include nuclear radiation resistance, self-extinguishing characteristics, chemical resistance, and good electrical properties. Nevertheless, the polyimides exhibit relatively low glass transition temperatures which cause thermoplastic failure at elevated temperature under stress. The maximum operating temperature for prolonged periods of time (<200 hours) is 600°F.

Many of the commercially available polyimides contain a small amount of cross-linking agent which slightly improves resin performance at elevated temperatures. The polyimides are not as hydrolytically stable as other members of the polyheterocyclic class. The hydrolytic instability is inherent in the imide ring and, therefore, impossible to alleviate completely. Degradation from ultraviolet radiation is a common problem associated with polymers and is also present with the polyimides. Future research may minimize ultraviolet deterioration but will not probably do away with it entirely.

A great deal of applications research, especially in the film and fiber area, is still being performed on the polyimides, primarily by DuPont and Monsanto. No recent published data on polyimide fiber properties are available. However, the polyimide fibers are expected to exhibit better properties than DuPont's aromatic polyamide fiber Nomex, which has potential application in many areas where fibrous materials are exposed to elevated temperatures. The polyimides form excellent films, having high tensile strength at room temperature (22,000 psi) and 390°F (12,000 psi).¹⁶

A limited amount of work on fabricating composites which incorporate polyimides is still being pursued by companies such as Bloomingdale, Brunswick, and Boeing. There does not appear to be any active Government-sponsored work on the polyimides, although a major portion of the initial research and development work was sponsored by the Air Force Materials Laboratory.¹⁷⁻¹⁹ ???

POLYBENZIMIDAZOLES

Polybenzimidazoles were the first members of the class of heterocyclic polymers to gain wide recognition in recent years as high-temperature resins. ?? They show considerable promise, not only as a matrix for high-temperature structural composite materials, but also as fibers and films. Considerable effort is being expended to determine processing parameters for optimum performance in the three forms. Polybenzimidazoles also show outstanding promise as ablative materials for low-density heat shields.

The fiber forming properties of the polybenzimidazoles, coupled with their very dense char forming properties upon pyrolysis, make them potential replacements for rayon as the basis for carbon fibers. The present cost of the raw materials is an obstacle to this application, however.

Certain film forming modified aliphatic polybenzimidazoles have recently found acceptance as separators in heat-sterilizable batteries, thus fulfilling a pressing need in the current space program.²⁰

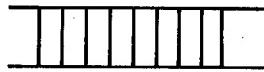
Polybenzimidazoles possess two properties which make them vitally important. First, the polymers have high decomposition temperatures (900°-1100°F) and good oxidation resistance. Second, they maintain excellent strength (5000-psi tensile shear at -360°F) at cryogenic temperatures. Research currently under way²¹ indicates that the oxidation resistance of these polymers can be improved to the point where they will be equal or superior to the best alternative polyheteroaromatic. It is anticipated that current research on polybenzimidazole will definitely yield a greatly improved polymer. This polymer class offers versatility in structure and synthetic methods not common to other new thermally stable polymers.

LADDER AND STEP LADDER POLYMERS

Nonrandom network polymers offer excellent potential for present and future aerospace applications. A representative of the class of nonrandom network polymers is the double chain or ladder polymer. To date, attempts to synthesize some of these polymers have resulted in only intractable materials, and the partial ladder or step-ladder polymer is employed as a compromising structure to obtain tractability. These structures can be represented as



Simple Linear Polymer



Ladder Polymer



Step-Ladder Polymer



Random Network

In fiber and film applications, the ladder systems are theoretically attractive since a minimum of two bonds in the chain must suffer cleavage before there is any loss in molecular weight. This feature is discussed in "Theoretical Studies on the Thermal Degradation of Ladder Polymers."²² In practice, increased chemical stability was noted for the polyphenylsilsesquioxanes,²³ and excellent radiation resistance was noted for the pyrrone step-ladder polymer.²⁴

A number of these ladder polymers have been synthesized and the majority have not been evaluated for applications use. The polyphenylsilsesquioxanes, evaluated as films by the Air Force, were found to have poor adhesive properties. Reference 23 contains a review of nonrandom network polymers.

POLYXYLYLENES

Poly-p-xylylenes are produced commercially by Union Carbide Corporation under the trade name Parylene. These polymers are prepared by the vapor phase polymerization of para-xylylene or substituted para-xylylenes to approximately 500,000 molecular weight. The principal advantages of these polymers are insolubility, excellent dielectric properties, low gas and vapor permeability, thermal stability in an inert atmosphere, and very high softening temperature.

At the present time, Union Carbide is the only organization currently conducting research on improving these polymers. This research is limited to its application as films and conformal coatings having an extremely high degree of uniformity. These polymers do not lend themselves to fiberization.

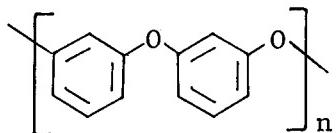
The polyxylylenes are unique in their ability to be used as conformal coatings on complex objects in thicknesses as low as 2 microns. They have good solvent resistance and extremely low moisture vapor transmission. These polymers are currently being used as dielectrics for rolled film capacitors, as coatings for miniature electronic components and circuit boards for protection against moisture and corrosive environments, as insulating and protective coatings for sensing probes, as photo-resistant coating, for solid state devices, in cryogenic memory circuits, and as windows for radiation measuring equipment. A possible application for these polymers in space is as a thin coating on the inside of condenser and heat exchanger tubes. The coating increases efficiency by 50%, thus effecting a great weight savings.

The most important disadvantages of the polymer are their poor oxidation stability, intractability, poor weathering, and high cost. In addition, the size of the object that can be coated is extremely limited. Since their introduction, polymers such as the polyaromatics and polyaromatic heterocyclics have shown equal or improved performance.

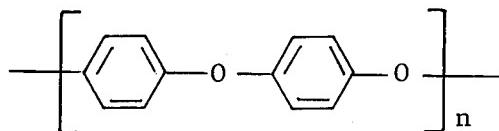
Besides the unsubstituted polyxylylene (Parylene N), there are two substituted polyxylylenes commercially available, polychloroxylylene (Parylene C) and polydichloroxylylene (Parylene D). These substituted polymers have a thermal resistance appreciably lower than the parent polymer, but they do have other properties which make them useful. It is probable that research can develop other substituted xylylenes which are more easily processed and which can be formed into fibers. It is also probable that films of the polymer could be fabricated in the vacuum environment of space.

POLYPHENYL ETHERS

The use of polyphenyl ethers such as I and II as a commercial thermoplastic,²⁵⁻²⁶ experimental high-temperature lubricant²⁷⁻²⁹ and hydraulic fluid applications³⁰ are fairly recent developments. There seems to be no active Government contracts for polyphenyl ether improvement or modification.



I. Poly-m-phenyl Ether



II. Poly-p-phenyl Ether

General Electric Company has recently marketed polyphenylene oxide 531-801 as an entirely new family of engineering thermoplastics. This polyphenylene oxide has a service temperature range from a brittle point of -275°F to a heat deflection point of 375°F (at 264 psi). It has exceptional resistance to hydrolytic breakdown and resistance to aqueous chemicals, steam, acids, and bases. Rigidity, dimensional stability, and toughness gives polyphenylene oxide excellent mechanical properties and very good electrical properties.

Commercial polyphenylene oxide was an outgrowth of materials developed by General Electric under Air Force Contract AF 33(616)7076. General Electric reported a single sample of poly-m-phenoxylenes, having a low functional group content, with a thermogravimetric analysis showing "outstanding thermal stability" (3% weight loss) up to 900°F. A molecular weight of 10,000 was the highest reported under this contract.

Dow Chemical has also been investigating polyphenyl ethers. Stamatoff²⁸⁻²⁹ has molded p-polyphenylene ether to produce a stiff film and has melt-drawn it into fibers, showing stability at 570°F for prolonged periods. It can be compression-molded at 390°-480°F into stiff, tough, transparent films that appear to be completely amorphous.

North American Aviation (Rocketdyne) is now working with a cross-linkable version of a polyphenylene ether.

POLYPHENYLENE

The Air Force Materials Laboratory is currently funding programs with Hughes³¹⁻³³ which include investigation of the polyphenylenes in ablative composites. Contractual work by the University of Maryland under Contract AF 33(657)7833 for the Aerospace Research Laboratories was finalized in March 1965. Their investigative efforts were restricted to cyclic polyphenylenes of eight rings or less.

The polyphenylene polymers, as a resin matrix, are of interest in space applications primarily for their ablative properties. They exhibit excellent char characteristics, thermal stability, and high resistance to oxidative and reductive environments. With polyphenylene, for example, there is less weight loss due to hydrocarbon fragmentation on exposure to high-temperature than with a phenolic system. However, polyphenylene systems are apparently needed which have higher molecular weights than 2000, which is now being obtained. Creep will occur above 480°F in present systems. If the molecular weight of polyphenylenes can be increased by either cross-linking or other effective measures, it is possible that their potential as fibers can be realized.

Future research directed toward the possible improvement of polyphenylene polymers should concentrate on increasing the molecular weight or cross-linking the polymers, investigating their fiber-forming potential, and developing suitable fabrication procedures. These efforts may improve the physical properties of the polymer.

A review of polyphenylene polymers and their physical characteristics³⁴ was published in a recent SAMPE journal.

SECTION IV

STRUCTURAL PROPERTIES OF SELECTED POLYMERS

The structural and physical properties of various polymer classes were compiled on the basis of film and fiber forms available. These forms, along with the molding compounds, represent the most frequently used processing form of the various polymers. The data for the polymers were obtained from many sources. Where possible, the manufacturer's data sheets were used for the information. Secondary sources included various handbooks, such as the Modern Plastics Encyclopedia and the Materials Selector.³⁵

As the literature of polymer properties was reviewed, it became evident that the polyolefin (polypropylene) had enough desirable properties, particularly low density to warrant continued investigation. However, it must be pointed out that extreme temperature ranges cause the fiber properties to degrade. At cryogenic temperature, for example, the fiber is brittle; at elevated temperature, the material decomposes.

Some information was not available for the various polymers. Several reasons apparently accounted for this lack of data. First, at the time of this writing the material was in early stages of development, so little engineering information was available. Polymers in the polyamide, polyheterocyclic, and polyaromatics classifications fell in this category.

A second reason for the lack of information is the proprietary nature of the various polymers. Manufacturers were invited to supply information on their products, but some were reluctant to do so because of their desire to protect the proprietary nature of the materials.

The lack of standard methods of evaluation for the different forms of the polymer also prevented incorporation of some of the available data. Only published test results which followed the standards established by the American Society for Testing and Materials (ASTM) were compiled for the evaluation.

Finally, the nonexistence of the polymer in a certain form (i.e., either fiber or film) would, of course, preclude the possibility of having information in this classification.

The data of the various polymers are presented in three groups. The first group lists the typical strength data for the polymers in molding or extrusion form. This is the most common form for the various polymers since the first applications were usually molded shapes. The second group presents the strength data for the polymer in film form. The third group provides the available strength data on fiber form of the material.

The structural properties for the polymers in molded forms are summarized in Table 5. The strength, ranges of modulus, and elongation of the material in the molded form are given in this table.

The forms in which the polymer is available is also listed in Table 5. The four forms of molding and extrusion compounds, film, and fiber represent basic products in which the polymers are available. Some of the polymers,

TABLE 5
GENERAL PROPERTIES OF SELECTED POLYMERS

Polymer Class	Chemical Name	Currently Available Forms	Molding Properties			
			Ult Tensile Strength, ksi	Modulus x10 ⁵ psi	% Elongation	Sp Gr, g/cm ³
Polyesters (Saturated)	Polyethyleneterephthalate	Film, fiber, molding	0.8-1.8* (6.0-13.0)	3.0-6.4	40-310 < 5	1.01-1.46
Polyamides	Polycaprolactam Nylon 6	Extrusion, film, fiber, molding	7-14	1.5-318	300	1.12-1.14
	Polyhexamethyleneadipamide Nylon 6/6	Extrusion, film, fiber, molding	11.8	--	60	1.14
	Polyhexamethylenesabacamide Nylon 6/10	Extrusion, film	7.0-8.5	1.6-1.9	320-85	1.09
	Poly-11-aminoundecanoic acid Nylon 11	Extrusion, molding	8.5	1.8-1.9	100-120	1.1
	Special mixed systems	Extrusion, molding	--	--	--	--
	Aromatic polyamides	Fiber	--	--	--	--
Polyfluorolefins	Polytetrafluoroethylene	Film, fiber, molding	2-4.5	0.58	200-400	2.13-2.22
	Copolymer of tetrafluoroethylene and hexafluoropropylene	Film, fiber	2.7-3.1	0.5	250-330	2.12-2.17
	Polychlorotrifluoroethylene	Film, molding	4.5-6.0	1.5-3.0	80-250	2.1-2.2
	Copolymer of tetrafluoroethylene and vinylidene fluoride	Film	--	--	--	--
	Polyvinylidene fluoride	Extrusion, molding	7.0	1.2	100-300	1.76-1.77
	Polyvinyl fluoride	Film	--	--	--	--
Regenerated Cellulose	Cellulose (Glucose- β -glucoside)	Film, fiber	--	--	--	--
Polyurethanes		Extrusion, film, fiber, molding	5-8	--	--	1.2-1.26
Ladders, Step Ladders	Poly-bis(benzimidazo)-benzodipyrrolidone	Film, molding	--	--	--	--
Polyheterocyclics	Polyimide Polybenzimidazole	Film, molding Film, fiber	10.5 --	4.5 --	6-7 --	-- --
Polyaromatics	Polyphenylene	Molding	--	--	--	--
	Polyxylylene	Film	--	--	--	--
	Polypropylene ether**	Extrusion, molding	10-11	3.6-3.8	50-80	1.06
Polyolefins	Polypropylene	Extrusion, film, fiber, molding	2.9-5.5	1.0-2.25	200-700	0.903-0.908

* Range from flexible to rigid, depending on processing techniques.
Parenthetical values are for rigid materials.

** Information from Reference 29.

such as the polyamide, polyurethane, and polyolefin groups, are available in all four forms. Other polymers, such as the aromatic polyamide and polyvinyl fluoride, were developed as a specific form (fiber and film respectively).

The materials available in fiber or film form were compiled in Tables 6 and 7, respectively. The data in these tables represent the strength of the various polymers as currently reported. The range of values in both tables indicates the minimum and maximum values reported in literature. There is no direct correlation between the strength level, for example, and the processing technique used for the material form. As a result, this information must be regarded only as a trend.

The properties of the fibers, as presented in Table 6, includes the strength, modulus, toughness, and elongation for the materials. All the properties were for room temperature and standard environment.

The term toughness has been defined as that area under the load-deformation curve. This value, while difficult to determine because of the lack of a standard method of evaluation, appears to be an increasingly important property for polymeric fibers. The toughness is a measure of the energy the fiber can absorb before failure. The use of polymeric fibers in space vehicles may very well depend on the toughness for a particular application. This discussion will be expanded upon later.

Other parameters for the fibrous material, such as strength and modulus, are normal in definition, and their importance in materials selection and structural analysis are well known.

The film materials information compiled in Table 7 was also based on room temperature and environment. In addition to the strength characteristics, the permeability to water vapor and certain gases was reported. For the film materials, a dual function application was assumed. The material is (1) either impervious, or at least has a low permeability to gases, and (2) the film material is carrying a load. The film materials can react tensile loads due to either pressure or axial conditions. Because of the inherent flexibility, films cannot support compressive loads without stabilization.

Specific values were plotted to obtain comparative values for the tensile strength and modulus of the various polymers. The specific tensile strength and modulus are shown in Figures 1 and 2, respectively. The specific strength was defined as the ultimate or breaking strength of the polymer divided by the density. Similarly, the specific modulus was defined as the reported modulus, usually in the elastic range of the material, divided by the density. For the figures, the specific gravity was converted to density; hence, the units for the values was the reciprocal of inches.

The shaded areas in Figures 1 and 2 represent the range of specific strength and modulus values reported in literature. The three different forms of molding compounds, film, and fiber are shown for each of the polymer classes. The polyester materials clearly show the difference in strength properties between the three different forms. The materials with only one form are also shown on the figures.

TABLE 6

PROPERTIES OF POLYMER FIBERS
ROOM TEMPERATURE AND AIR ENVIRONMENT

Polymer Class	Chemical Name	Fibrous Form	Ult. Tensile Strength, kst	Modulus, x10 ⁶ psi	Stiffness, g/denier	% Elongation	Toughness, g/cm ² diameter/cm	Sp. Gr., g/cm ³	Strain Recovery @ 2%	Source
Polyesters (Saturated)	Polyethylene terephthalate	Staple Filament	67-76 77-123	1.9-1.99	24-65	30-36 9-25	0.50-0.78	1.03 1.38	-- --	Materials Selector
Polyamides	Polycaprolactam Nylon 6	Staple Filament	70-80	--	17-20	37-40	0.64-0.78	1.14	100	
	Polyhexamethylene diphamide Nylon 6/6	Staple Filament	58-69 67-128	0.5-0.66	23-48 10 18-32	16-34 38-42 18-32	0.67-0.75 0.87 0.76-85	-- -- 1.14	-- -- --	
	Polyhexamethylene sebacamide Nylon 6/10	--	--	--	--	---	--	--	--	
	Poly-11-aminoundecanoic acid Nylon 11	--	--	--	--	--	--	--	--	
	Special mixed systems	--	--	--	--	--	--	--	--	
	Aromatic polyamides	Yarn	95	2.51	--	17	0.69	--	--	
Polyfluorolefins	Polytetrafluoroethylene	Filament	47	--	12	13	0.12	1.38	--	DuPont NP 33, Properties of Teflon High-Temp Assistance Nylon Sheet
	Copolymer of tetrafluoro- ethylene and hexafluoro- propylene	--	--	--	--	--	--	--	--	
	Polychlorotrifluoroethylene	--	--	--	--	--	--	--	--	
	Copolymer of tetrafluoro- ethylene and vinylidene fluoride	--	--	--	--	--	--	--	--	
	Polyvinidene fluoride	--	--	--	--	--	--	--	--	
	Polyvinyl fluoride	--	--	--	--	--	--	--	--	
Regenerated Cellulose	Cellulose (Glucose-β-D-glucoside)	Filament Filament	136 65-105	--	117 25.5-29	6 9-22	0.21 0.22-0.30	1.5 ≈1.5	--	Fortisan Rayon
Polyurethanes	--	--	--	--	--	--	--	--	--	
Ladders, Step Ladders	Poly-bis(benzimidazole)- benzodipyrrolidone	--	--	--	--	--	--	--	--	
Polyheterocyclics	Polyimidide Polybenzimidazole	Yarn	75-79	1.64-1.9	--	--	--	≈1.32	--	Reference 36
Polyaromatics	Polyphenylene Polyphenylene ether	-- --	-- --	-- --	-- --	-- --	-- --	-- --	--	
Polyolefins	Polypropylene	Filament	45-102	--	6.8-14.2	--	--	0.90	--	

TABLE 7

PROPERTIES OF POLYMER FILMS
ROOM TEMPERATURE AND AIR ENVIRONMENT

Polymer Class	Chemical Name	Ult. Tensile Strength, ksi	Tensile Modulus, $\times 10^5$ psi	% Elongation	Burst Strength (Mullen) psi	Fold Endurance, cycles	Water Vapor Permeability, g/100 in. ² /24 hr/mil	Gas Permeability, cm ³ /100 in. ² /24 hr/mil		Service Temp Min./Max., °F	Sp. Gr., g/cm ³	Source
								O ₂	N ₂			
Polyesters (Saturated)	Polyethylene terephthalate	25-40	5.5-8.0	120-50	55-66	14,000	1.8	6	1	16	-75/-4300	1.395-1.377
Polyamides	Polyacrylamide	13.8-17	--	>200	--	Excellent	0.9-1.0	6.5	0.7	11	-100/+380	1.12
	Nylon 6	12	--	>250	--	Excellent	--	2.5	--	--	-100/+300	1.14
	Polyhexamethylene adipamide	10	--	>250	--	Excellent	--	4.5	--	--	--	Materials Selector
	Polyhexamethylene sebacamide	--	--	--	--	--	--	--	--	--	--	Materials Selector
	Nylon 6/10	--	--	--	--	--	--	--	--	--	--	Materials Selector
	Poly-11-aminoundecanoic acid	--	--	--	--	--	--	--	--	--	--	Materials Selector
	Nylon 11	--	--	--	--	--	--	--	--	--	--	Materials Selector
	Special mixed systems	--	--	--	--	--	--	--	--	--	--	Materials Selector
	Aromatic polyamides	--	--	--	--	--	--	--	--	--	--	Materials Selector
Polyfluorolefins	Polytetrafluoroethylene	4	--	>270	--	--	--	--	--	--	--	--
	Copolymer of tetrafluoroethylene and hexafluoropropylene	3-3.5	--	300-400	10-15	4,000	0.4	950	360	1850	-400/+400	2.15
	Polychlorotrifluoroethylene	5-8	--	50-150	23-31	Good	0.25	7-12	2.5	16-40	-320/+390	2.1
	Copolymer of tetrafluoroethylene and vinylidene fluoride	--	--	--	--	--	--	--	--	--	--	Materials Selector
	Polyvinylidene fluoride	--	--	--	--	--	--	--	--	--	--	Materials Selector
	Polyvinyl fluoride	13.7-19.1	2.8	110-185	37-70	15,000-37,000	3.24	3.2	0.25	15	-100/+225	1.53-1.38
Regenerated Cellulose	Cellulose (Glucose- β -Glucoside)	18	--	16-17	46-69	13,000	1.34	1.7	2.7	39	--	--
Polyurethanes		5-6	--	>400	--	--	4.5-15	--	--	--	1.24-1.26	Bull. G-27, Ectane Polyurethane Material, BF Goodrich
Ladders, Step Ladders	Polybis(benzimidazo)-benzodipyrrolidone	15-22	6-10	3-7	--	\	--	--	--	--	1.3-1.4	NASA TN-D3148
Polyheterocyclics	Polyimide	19.5	4.3	128	75	10,000	--	--	--	--	1.42	Reference 37 and H-film data, DuPont
	Polybenzimidazole	--	--	--	--	--	--	--	--	--	--	--
Polyaromatics	Polyphenylene	--	--	--	--	--	--	--	--	--	--	Modern Plastics Encyclopedia
	Polyxylylene	9-13	3.5-4.0*	200	--	--	14 (N)*†	30 (N)	225 (N)	--	1.103-1.120	--
	Polyphenylene ether	10-11	3.6-3.8	50-80	--	--	1 (C)	5 (C)	12 (C)	--	--	--
Polyolefins	Polypropylene Biaxially oriented	24-33	--	60-90	--	Excellent	0.36-0.45	105-150	10-25	300-500	--	0.902-0.907

* Secant.

** The letters N and C are used to identify two types of polymer.

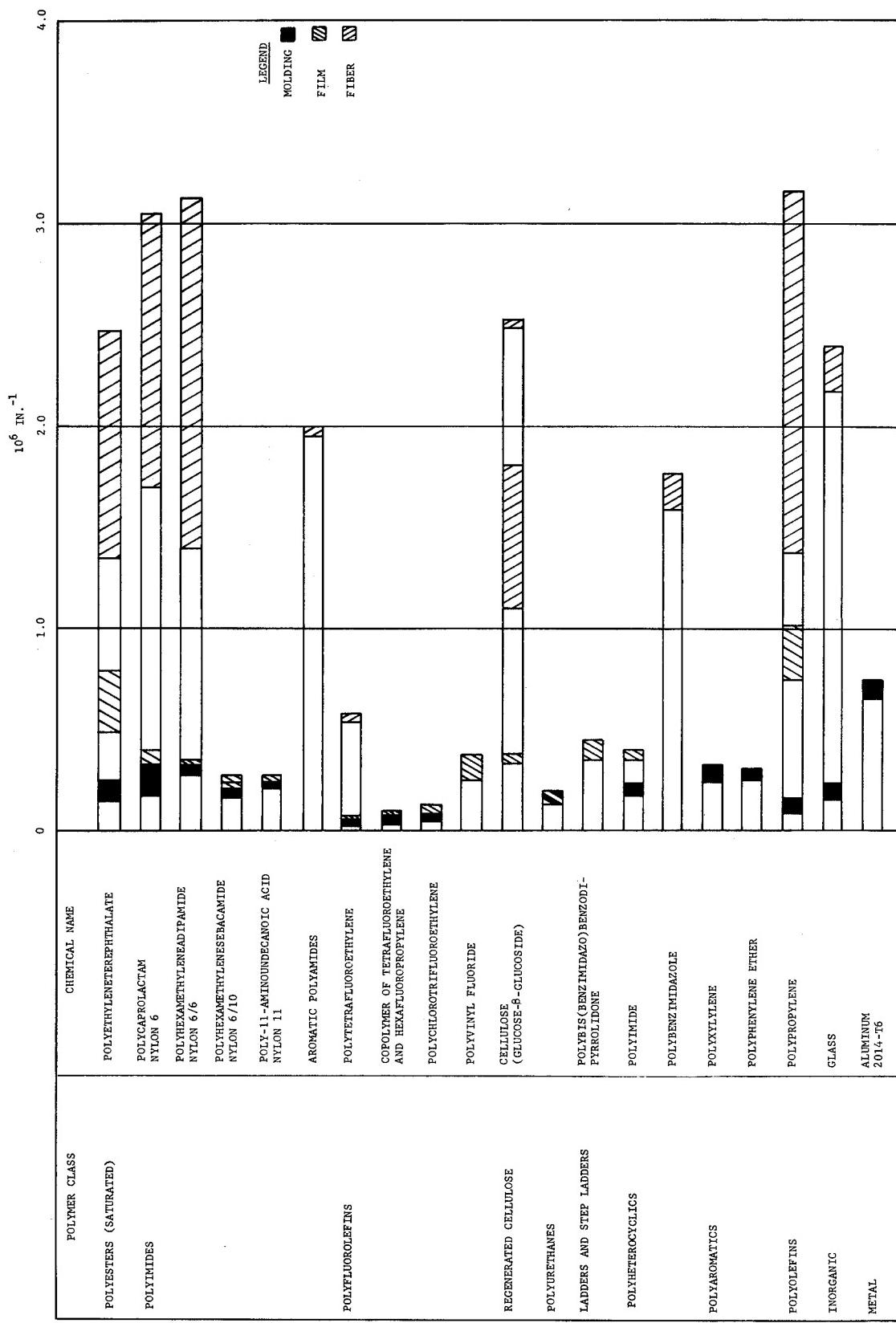


Figure 1. Strength of Various Polymers

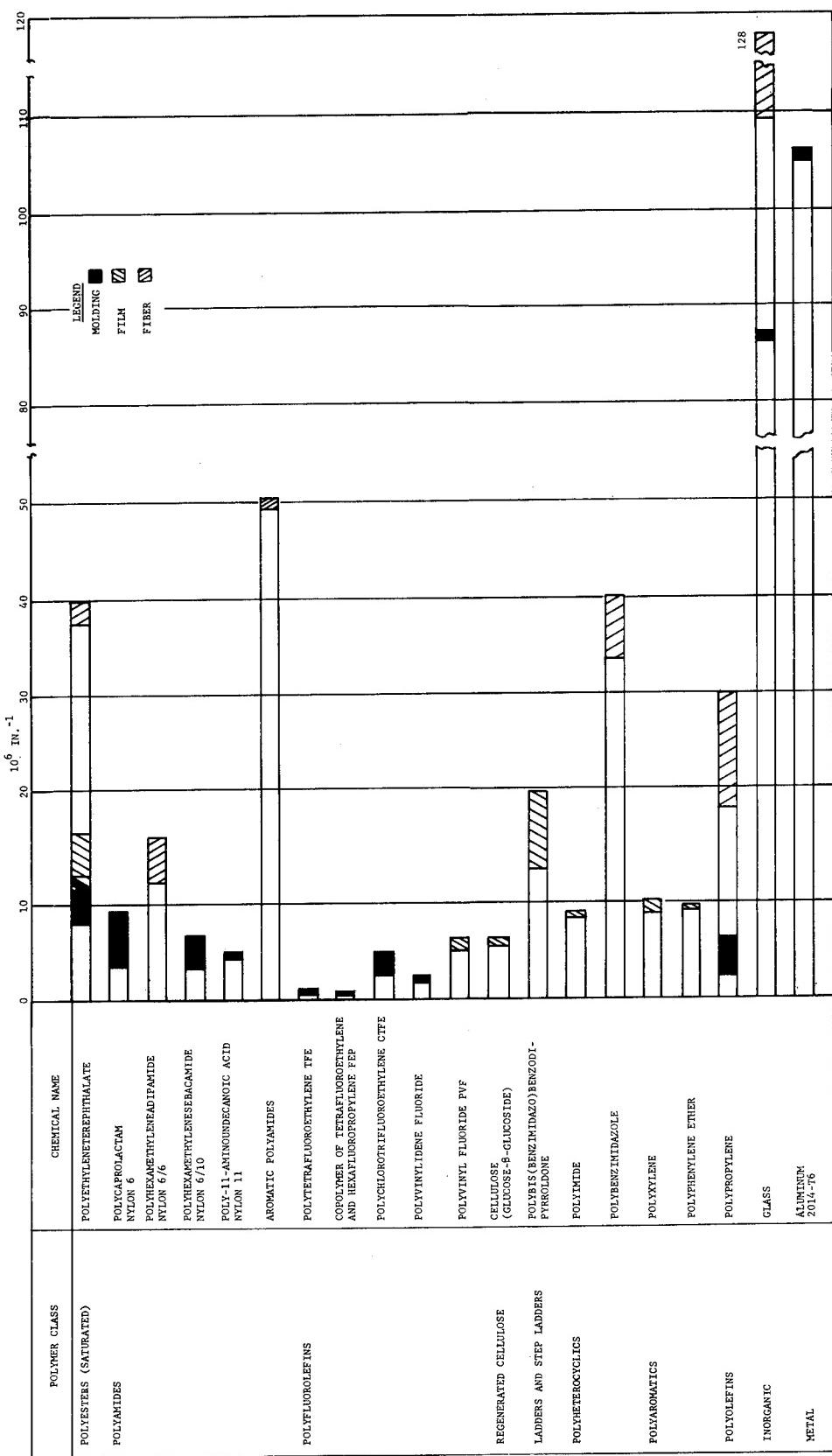


Figure 2. Specific Tensile Modulus for Various Polymers

Four polymers exhibited the greatest combined specific strength and modulus values particularly in fiber form. The polymers included polyethylene-terephthalate, aromatic polyamide, polypropylene, and polybenzimidazole. The first three of these four materials are currently available while the last is in the advanced development stage. It is interesting to note that the fibrous form of the aromatic polyamide and polybenzimidazole materials have a small spread in both strength and modulus when compared to the other two materials. Aromatic polyamide has a slight advantage over polybenzimidazole for room temperature applications; however, the latter material may be better for elevated temperature space applications.

Some materials, particularly those in the regenerated cellulose and polyamide classes, exhibit relatively high room temperature specific strength but low modulus values. These two materials also had a wide range of reported test values, indicating that the form of polymers is changed through the technique used by the processor when he draws the fiber. This range may be attributable to different grades of the material, specifically formed for different applications and on the basis of economic considerations.

The low moduli of regenerated cellulose and polyamide polymers are indicative of the material's flexibility. These materials may be used to advantage in applications where material flexibility is desirable, such as for decelerators.

Little information was available on the fibrous form of the remaining materials. The materials are generally made in the bulk or film form and are characterized by properties other than strength (e.g., films for gas retention). The polyfluorolefins and polyaromatics classes fall in this category of materials. The ladder and step ladder class of materials has been produced only in film form, with a rather unique characteristic of relatively high specific modulus but low tensile strength. While data were not reported because the polymer either has not been made in fibrous or film forms or is in very early development stages, the materials may hold potential for structural application because of the relatively high bulk strength and modulus values. The selected polymers of the ladder and step ladder, polyheterocyclic, and polyaromatic classes fall within this potential application area.

SECTION V

POTENTIAL OF THE SELECTED POLYMERS

Polymer applications will depend on the interplay of many factors, including material properties, environment, design criteria, weight, and cost. Because many polymeric or even composite materials may be tailored to a particular application, the interaction of material properties and design will become increasingly important. For example, the design criteria determines the basic loads, while the geometry is constrained by size limitation or functional requirements. The composite material is then tailored to the criteria to provide the required strength and stiffness of the part. This same approach should be used to determine the potential of the various materials to space applications.

The usefulness of tailoring the polymeric materials to specific applications is also one of the reasons for such a wide variation in properties for a given material. A slight change in chemical formulation for one polymer may provide an entirely different compound with unique properties. This wide variation of material characteristics complicated attempts to attain one of the major objectives for this program: that of establishing a handbook of information.

The material which can be readily formed into films or fibers will probably hold the most promise for space applications. The term readily formed must also apply to the polymeric materials which are in the development stage at this writing. The polymer in fiber or film stage has better specific strength than the bulk form of the material; hence, lower structural weight may ensue.

Each form of the material has some general unique properties. For example, the fiber is unidirectional and must therefore be placed in the direction of the maximum load component. For an orthotropic loading condition, the fiber may be either laminated in sheets or woven into cloth in order to orient the material in the two directions.

On the other hand, a film is considered to be biaxial in nature and carries a lower load in any direction in the plane of construction. The film carries load only in a tensile condition; that is, either by axial tension or membrane action. The film is continuous and is used as a barrier for gas or fluid.

The structural capabilities of the various polymers lie in the areas of tension structures. The specific tensile strength of the various selected polymers was found to be comparable with that of glass fibers or bulk aluminum, whereas the specific modulus was much lower than that of glass fiber. The tension structures generally do not require material stiffness to perform their function.

Some of the polymers discussed in this report may, with further development, meet some of these general requirements for space structures. The effect that space environment has on the polymer's structural potential will have to be established.

Some of the potential means for modifying polymers to improve properties in the space environment, discussed in the preceding text, are summarized below.

Polyester. Structural modification will not improve the thermal stability of polyester. Improved resistance from ionizing radiation may be accomplished by the use of cyclic diols.

Polyamides. The aromatic polyamides are probably close to the ultimate molecular structure for temperature and radiation resistance.

Regenerated Cellulose. This material is also approaching the probable limit for resistance to space environment, although improvement of room temperature properties may be possible.

Polyurethane. Elevated temperature properties may be improved at the expense of low temperature properties. The fluorinated polyurethane may have greater heat and radiation resistance than conventional polyurethanes.

Polyimides. The polymer has features which make attractive for potential space application; e.g., nuclear radiation resistance, self extinguishing characteristics, and elevated temperature capability. In its present form, the polymer degrades from ultraviolet radiation. The polymer may have potential in a structural fiber form.

Polybenzimidazoles. Current efforts in the fiberization of this polymer may yield fibers for potential space application. The polymer has characteristics similar to the polyimides.

Polyfluorolefins. This polymer has the best potential as a coating material. The polymer has moderate elevated temperature capability. The greatest potential for space applications appears to rise from its low surface friction characteristics.

SECTION VI

CONCLUSIONS

During this investigation, many interesting aspects of utilizing polymeric materials for space application revealed themselves. They range from material properties to methods of analysis for applying polymers to space applications. The following items enumerate the pertinent points of the investigation:

1. The specific fiber strength of the polyester, some polyamides, regenerated cellulose, and polypropylene are in the same range as or exceed the fibrous glass specific strength.
2. The newer polymer classes such as the polyheterocyclics, polyaromatics, and ladders have the potential to match or exceed the specific strength of fibrous glass. However, the polymers will have to be further developed in order to draw experimental fibers. These materials, from the limited information available have higher bulk strength than the other selected polymers.
3. The specific tensile modulus of all the polymers is much less than fiber-glass. The polymer classes which had information available were on the order of 50% the specific strength of the fiberglass. No conclusions could be made on the newer material because of insufficient information. However, based upon the strength characteristics an improvement in specific modulus may be expected.
4. Minimal information was available on the effect of the space environment upon the various polymer materials. The polyester, polyamide, and poly-fluorolefins classes had most of the reported data on the effect of vacuum, ultraviolet and particle radiations. At this time, the polymers with high-temperature capabilities also appear to be structurally stable in the space environment.
5. According to literature, the use of polymers for reinforcement is still in very early stages. The use of polymer fibers in composite may present a new group of engineering materials with high toughness characteristics. Typical laminates of these materials may include combination of polyester, polyamide, polyimide, polyheterocyclic, and polyaromatic polymers.
6. The use of polymeric materials for reinforcement requires improved methods of analyzing the results of tests and also evaluating composites for various applications. The use of toughness parameter of the polymer may provide a means to evaluate the material and composite properties. The use of the area under the load-deformation curve as the measure of toughness is a starting point for this type of analysis.

The application of the polymeric material is dependent upon the loading rate. For example, toughness or area under the load-deformation curve is much greater for high loading rates than for low loading.

Through the knowledge of the loading rate the amount of load capable of being reacted by the composite will be established. This method of analysis

will be patterned after the strain energy methods of analysis. The use of the toughness criteria will allow the material to be fully tailored to the application. This approach will be particularly advantageous to polymeric materials which have higher elongation than the materials currently in use. The possible applications where the toughness analysis will be used include the structures where elongation is either permissible or desirable.

7. The use of a greater variety of polymers for space application appear to be feasible. Polymer fibers and films will be useful for both rigid and flexible applications. The flexible material application would cover expandable structure and decelerators. The use of polymeric materials for reinforcement could include energy absorption structures and primary load-carrying structures such as composite panels and filament-wound storage vessels.

8. The standardization of test techniques is required in order to better correlate the test data from many sources.

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APPENDIX

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